PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08L 75/04, 69/00

A1

(11) International Publication Number: **WO 97/19995**

(43) International Publication Date: 5 June 1997 (05.06.97)

(21) International Application Number: PCT/IL96/00165

(22) International Filing Date: 24 November 1996 (24.11.96)

(30) Priority Data:
116192 29 November 1995 (29.11.95) IL

(71) Applicant *(for all designated States except US)*: PALTOUGH LTD. [IL/IL]; 30035 Ramat Yohanan (IL).

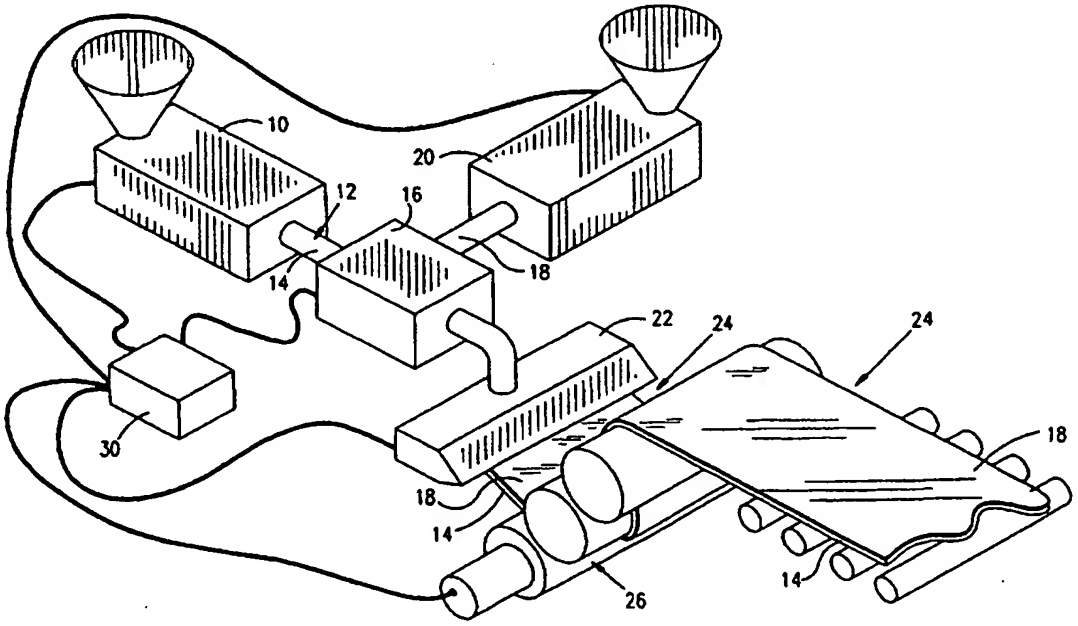
(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: BEN ZVI, Guy [IL/IL]; 30035 Kibbutz Yohanan (IL).

(74) Agents: SANFORD, T., Colb et al.; Sanford T. Colb & Co., P.O. Box 2273, 76122 Rehovot (IL).

(81) Designated States: AU, CA, CN, JP, NO, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: EXTRUDED PLASTIC



(57) Abstract

An extruded plastic product formed of rigid thermoplastic polyurethane.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	**GB**	United Kingdom	**MW**	Malawi
AT	Austria	**GE**	Georgia	**MX**	Mexico
AU	Australia	**GN**	Guinea	**NE**	Niger
BB	Barbados	**GR**	Greece	**NL**	Netherlands
BE	Belgium	**HU**	Hungary	**NO**	Norway
BF	Burkina Faso	**IE**	Ireland	**NZ**	New Zealand
BG	Bulgaria	**IT**	Italy	**PL**	Poland
BJ	Benin	**JP**	Japan	**PT**	Portugal
BR	Brazil	**KE**	Kenya	**RO**	Romania
BY	Belarus	**KG**	Kyrgystan	**RU**	Russian Federation
CA	Canada	**KP**	Democratic People's Republic of Korea	**SD**	Sudan
CF	Central African Republic			**SE**	Sweden
CG	Congo	**KR**	Republic of Korea	**SG**	Singapore
CH	Switzerland	**KZ**	Kazakhstan	**SI**	Slovenia
CI	Côte d'Ivoire	**LI**	Liechtenstein	**SK**	Slovakia
CM	Cameroon	**LK**	Sri Lanka	**SN**	Senegal
CN	China	**LR**	Liberia	**SZ**	Swaziland
CS	Czechoslovakia	**LT**	Lithuania	**TD**	Chad
CZ	Czech Republic	**LU**	Luxembourg	**TG**	Togo
DE	Germany	**LV**	Latvia	**TJ**	Tajikistan
DK	Denmark	**MC**	Monaco	**TT**	Trinidad and Tobago
EE	Estonia	**MD**	Republic of Moldova	**UA**	Ukraine
ES	Spain	**MG**	Madagascar	**UG**	Uganda
FI	Finland	**ML**	Mali	**US**	United States of America
FR	France	**MN**	Mongolia	**UZ**	Uzbekistan
GA	Gabon	**MR**	Mauritania	**VN**	Viet Nam

EXTRUDED PLASTIC

The present invention relates to extrusion of plastic materials and more particularly to extrusion of transparent plastic materials.

Various types of extruded transparent plastic materials are known. Extruded polycarbonate is well known and used for a wide variety of applications. Various types of extruded polycarbonate sheets are manufactured and sold under the PALTOUGH trademark by the present applicant/assignee.

When combined with a UV protector, such as taught in European Patent 0247,480, polycarbonate displays good UV resistance.

Polycarbonate is considered to have limited resistance to attack by chemical agents, including those in the atmosphere.

The present invention seeks to provide an improved extruded plastic product which displays high resistance to chemical agents.

There is thus provided in accordance with a preferred embodiment of the present invention an extruded plastic product formed of rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

There is also provided in accordance with a preferred embodiment of the present invention an extruded plastic product formed of coextruded polycarbonate and rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

There is additionally provided in accordance with a preferred embodiment of the present invention an extruded plastic sheet formed of thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

There is further provided in accordance with a

preferred embodiment of the present invention an extruded plastic sheet formed of coextruded polycarbonate and thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

Additionally in accordance with a preferred embodiment of the present invention there is provided a method of producing a plastic product comprising extruding a rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

Further in accordance with a preferred embodiment of the present invention there is provided a method of producing a plastic product comprising coextruding polycarbonate and rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

Still further in accordance with a preferred embodiment of the present invention there is provided a method of producing a plastic sheet comprising extruding a rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

There is also provided in accordance with a preferred embodiment of the present invention a method of producing a plastic sheet comprising coextruding polycarbonate and rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin.

In the co-extruded products, preferably the thickness of the thermoplastic polyurethane is less than 50 microns.

Additionally in accordance with a preferred embodiment of the present invention the extruded products include a UV protective agent.

The present invention will be understood and appreciated more fully from the following detailed description, taken in conjunction with the drawings in which:

Fig. 1 is a simplified illustration of co-extrusion of plastic sheets in accordance with a preferred embodiment of the present invention;

Fig. 2 is a sectional illustration of a plastic sheet constructed and operative in accordance with a preferred embodiment of the present invention;

Fig. 3 is a simplified illustration of an extruded tank liner constructed and operative in accordance with a preferred embodiment of the present invention;

Fig. 4 is a simplified illustration of a billboard constructed and operative in accordance with a preferred embodiment of the present invention;

Fig. 5 is a table of test results of color parameters of a rigid thermoplastic polyurethane with different UV protectors at different concentrations at varying levels of UV exposure; and

Figs. 6 and 7 are graphical representations of some of the test results of Fig. 5.

Reference is now made to Fig. 1, which is a simplified illustration of coextrusion of plastic sheets in accordance with a preferred embodiment of the present invention. The coextrusion may be carried out using any suitable coextrusion apparatus, which preferably includes a primary extruder 10 for extruding a bulk sheet 12 of a first polymeric material 14, preferably polycarbonate, of thicknesses from 0.1 to over 15 mm.

A feed block 16 is preferably provided for combining bulk sheet 12 with a coextruded layer of at least another polymeric material 18. In accordance with a preferred embodiment of the present invention, the other polymeric material is a rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin. A coextruder 20 is preferably provided for extruding polymeric material 18.

A flat sheet die 22 is preferably provided for

extruding a flat sheet 24 of the coextruded polymeric materials 14 and 18, to the desired thickness and width. Alternatively, in place of coextruder 20 and flat sheet die 22, a multi-manifold die (not shown) may be used to combine two or more polymeric layers.

A calender system 26 is preferably provided for polishing the sheet 24. It is appreciated that other conventional equipment for producing flat plastic sheets may be added downstream of calender system 26. Alternatively, a calibrating or corrugating system (not shown) may be used in place of calender system 26, along with appropriate downstream equipment.

Preferably control apparatus 30 is provided for controlling various operations in the coextrusion process. Since ISOPLAST and polycarbonate, or other pairs of polymeric materials, are usually rheologically different, their coextrusion requires control of factors such as tool temperatures, melting temperatures and pressures, feed block flow design, start-up and shutdown conditions and pre-drying conditions. Control apparatus 30 preferably includes appropriate sensors for sensing and controlling factors such as the aforementioned.

Referring now to Fig. 2, there is shown in sectional illustration a plastic sheet 32 constructed and operative in accordance with a preferred embodiment of the present invention. Sheet 32 is seen to have a relatively thick portion 34, which is preferably formed of polycarbonate or other polymer, and a relatively thin portion 36, formed of rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin. Preferably the thickness of portion 36 is less than 50 microns.

According to an alternative embodiment of the present invention, rigid thermoplastic polyurethane, preferably ISOPLAST brand Engineering Thermoplastic Resin, may be extruded alone into sheets or other

products.

Additionally in accordance with a preferred embodiment of the present invention, a UV protective agent, such as benzotriazole, may be added to the extruded or co-extruded plastic in suitable proportions, typically about 10%.

Applicant has carried out several extrusion tests in the scope of the present invention. Some of these test include:

1. Mono-extrusion of ISOPLAST brand Engineering Thermoplastic Resin.

2. Coextrusion of one side of 10 - 100 microns of ISOPLAST brand Engineering Thermoplastic Resin on polycarbonate to find desirable thicknesses for good chemical protection combined with good optical and mechanical properties.

3. Detailed chemical resistance tests which resulted in a broad list of materials normally incompatible with polycarbonate and which are compatible with polycarbonate coextruded with ISOPLAST in accordance with a preferred embodiment of the present invention.

4. Detailed mechanical, thermal, optical and thermoformability tests of sheet coextruded in accordance with a preferred embodiment of the present invention.

5. Two-sided coextrusion of ISOPLAST brand Engineering Thermoplastic Resin on polycarbonate.

6. UV protection tests of UV absorbers in the coextruded layer. A significant improvement has been observed in the rate of yellowing under UV radiation. Results of these tests are shown tabularly in Fig. 5 and graphically in Figs. 6 and 7.

The yellowness tests were performed on three different UV absorbers, A, B and C, according to ASTM (American Society for Testing Materials) D1925 with a Q panel machine which complies with ASTM G53. As is known to persons skilled in the art, L*, a* and b* are color

coordinates according to CIE (Commission Internationale de l'Eclairage) 1931.

With proper control of the coextrusion process, a very clear, very tough and chemical resistant sheet may be produced. This sheet is also thermoformable to different articles, such as containers and cups, making it very useful for storing chemical fluids in tough, high temperature (above 100 degrees Celsius) and optically clear applications.

The polycarbonate and ISOPLAST coextruded sheet, constructed in accordance with a preferred embodiment of the present invention, allows the use of polycarbonate in many applications where its limited chemical resistance normally prevents its selection as a viable material. An example of such an application is shown in Fig. 3, which is a simplified illustration of an extruded tank liner constructed and operative in accordance with a preferred embodiment of the present invention.

In addition, the coextruded sheet of the present invention enhances the performance of polycarbonate in applications where polycarbonate alone is traditionally used. An example of such an application is shown in Fig. 4 which is a simplified illustration of a billboard constructed and operative in accordance with a preferred embodiment of the present invention. Here a transparent coextruded sheet 40 is disposed over the billboard poster for protecting it from the elements.

It will be appreciated by persons skilled in the art that the present invention is not limited by what has been particularly shown and described hereinabove. Rather the scope of the present invention is defined only by the claims which follow:

C L A I M S

1. An extruded plastic product formed of rigid thermoplastic polyurethane.

2. An extruded plastic product according to claim 1 and wherein said rigid thermoplastic polyurethane is ISOPLAST brand Engineering Thermoplastic Resin.

3. An extruded plastic product formed of coextruded polycarbonate and rigid thermoplastic polyurethane.

4. An extruded plastic product according to claim 3 and wherein said rigid thermoplastic polyurethane is ISOPLAST brand Engineering Thermoplastic Resin.

5. An extruded plastic product according to any of the preceding claims and wherein the thickness of the thermoplastic polyurethane is less than 50 microns.

6. An extruded plastic product according to any of the preceding claims and also including a UV protective agent.

7. A method of producing a plastic product comprising extruding a rigid thermoplastic polyurethane.

8. A method according to claim 7 and wherein said rigid thermoplastic polyurethane comprises ISOPLAST brand Engineering Thermoplastic Resin.

9. A method of producing a plastic product comprising coextruding polycarbonate and rigid thermoplastic polyurethane.

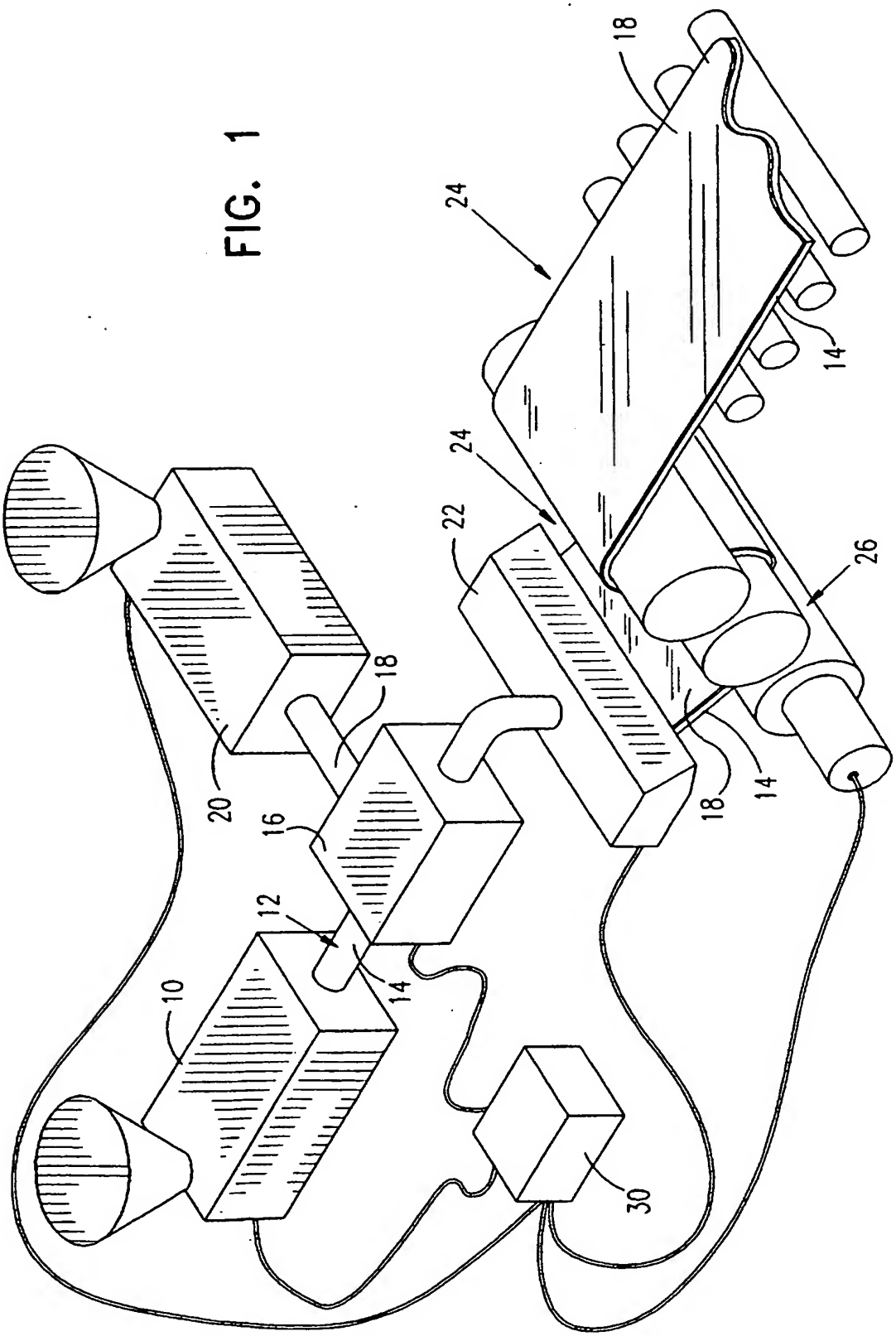
10. A method according to claim 9 and wherein said

rigid thermoplastic polyurethane comprises ISOPLAST brand Engineering Thermoplastic Resin.

11. A method according to any of claims 7 - 10 and wherein the thickness of the thermoplastic polyurethane is less than 50 microns.

12. A method according to any of claims 7 - 11 and also including the step of adding a UV protective agent prior to extrusion.

FIG. 1



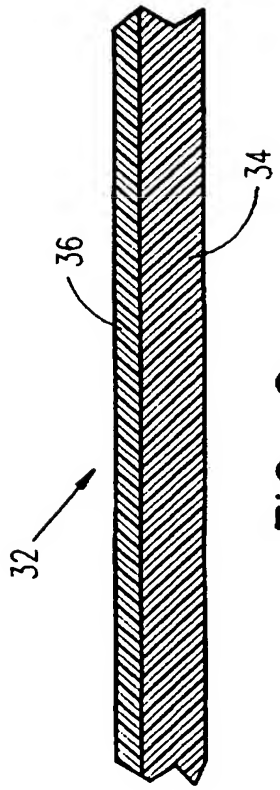


FIG. 2

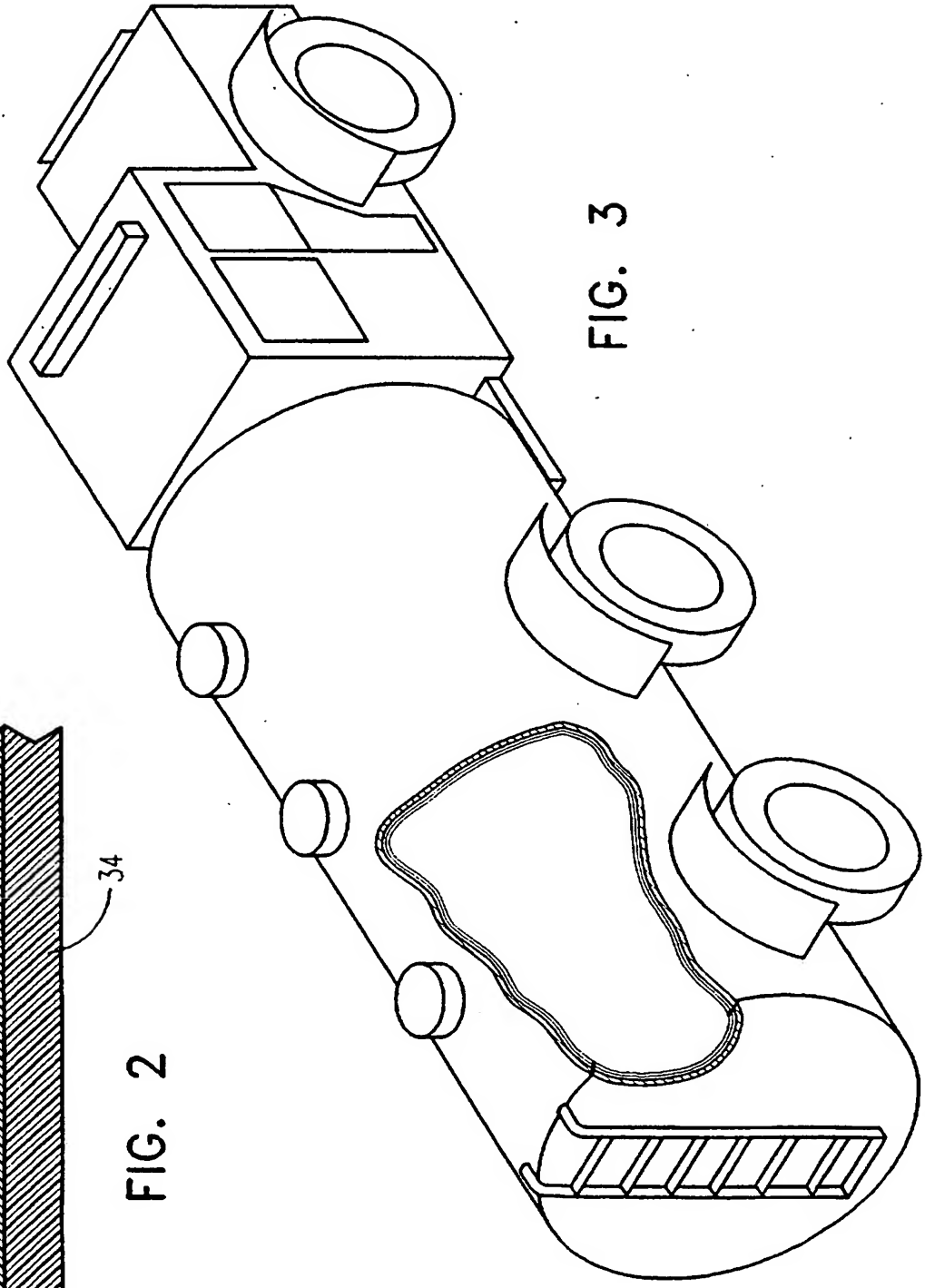


FIG. 3

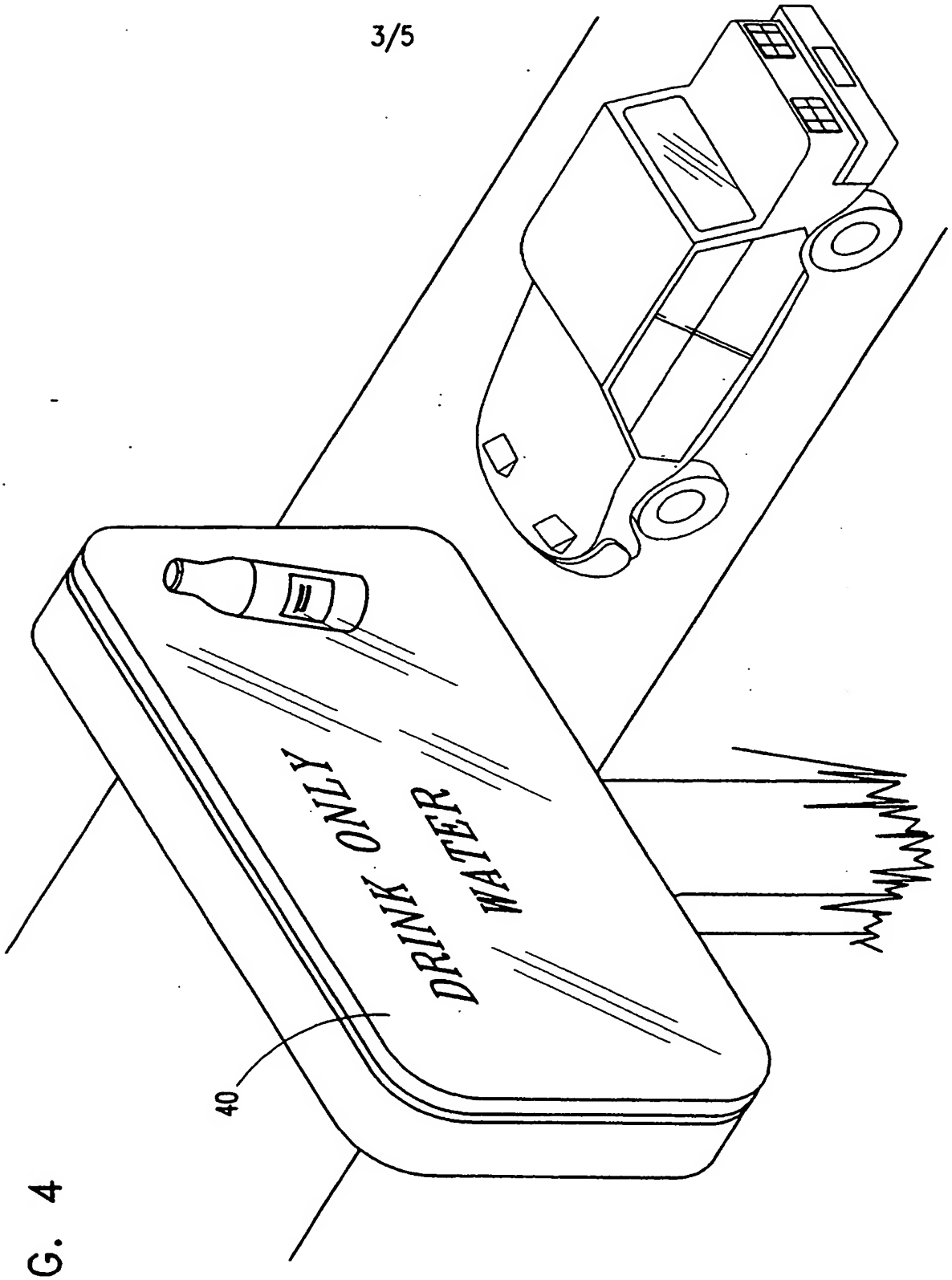


FIG. 4

TYPE	%UV	QUV HRS	L*	a*	b*	Yi	d-yi
A 0%		0	95.02	-0.35	1.03	1.74	27
A 0%		300	93.01	-4.31	17.67	28.78	
B 4%	*A*	0	93.24	-0.56	4.08	7.5	12
B 4%	*A*	300	91.95	-0.29	11.31	19.6	
B 7%	*B*	0	93.34	-0.29	2.88	5.41	10
B 7%	*B*	300	91.83	-1.83	8.77	15.39	
C 4%	*A*	0	91.39	-1.52	6.78	12.02	9
C 4%	*A*	300	89.97	-2.39	12.36	21.73	
C 7%	*B*	0	89.27	-2.66	12.97	22.74	7
C 7%	*B*	300	88.42	-3.26	17.28	29.94	
C 10%	*C*	0	88.55	-2.79	15.2	26.72	11
C 10%	*C*	300	86.51	-3.4	21.77	37.87	

FIG. 5

FIG. 6

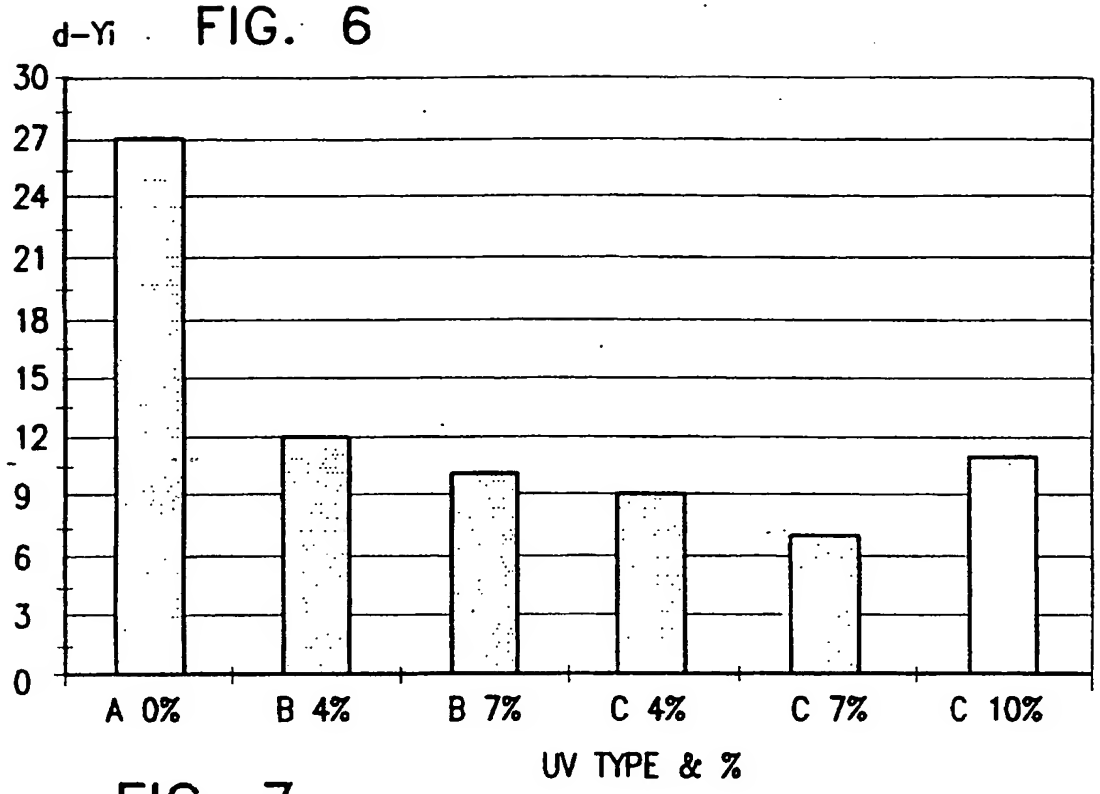
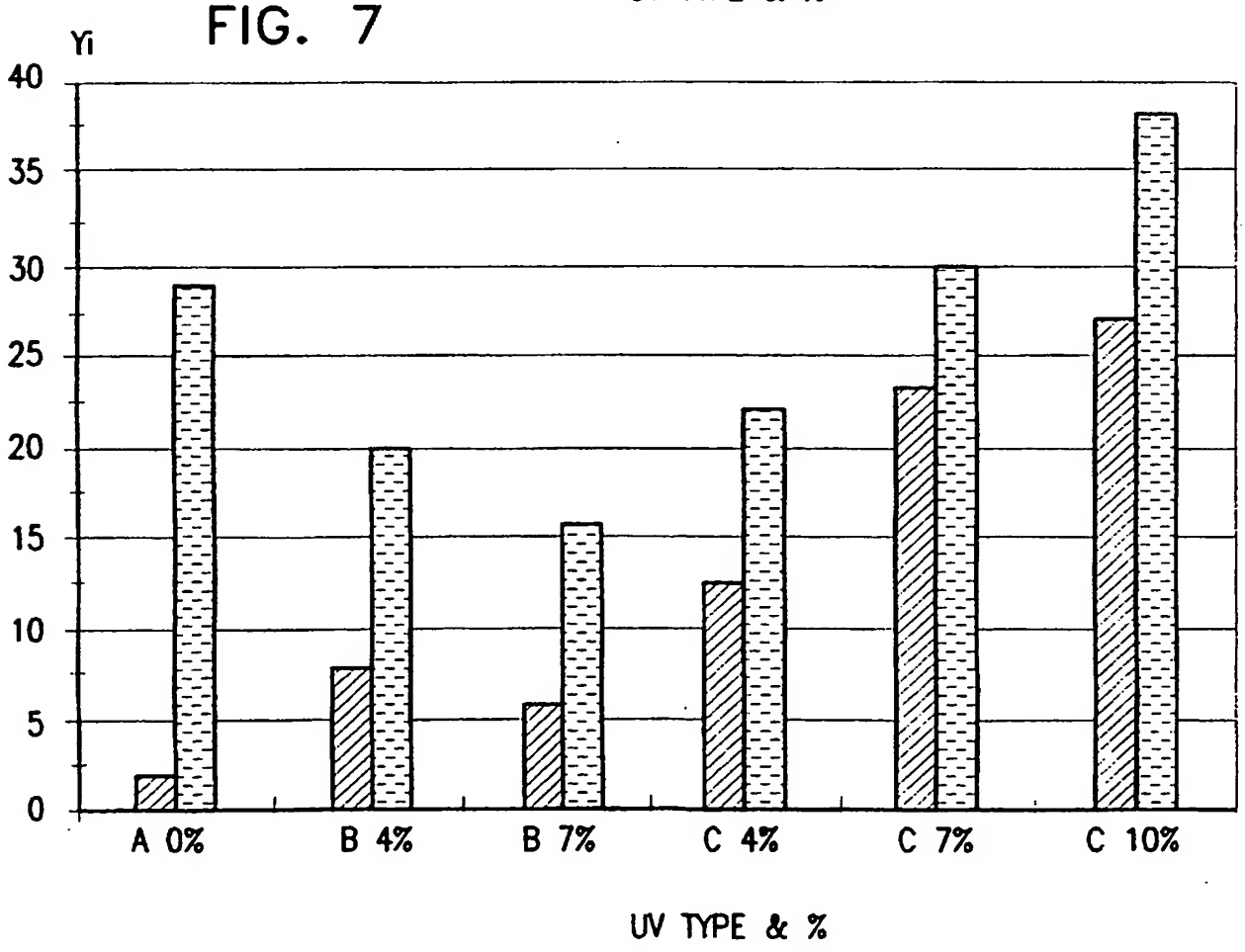

d-Yi
30
27
24
21
18
15
12
9
6
3
0
A 0%
B 4%
B 7%
C 4%
C 7%
C 10%
UV TYPE & %

FIG. 7


Yi
40
35
30
25
20
15
10
5
0
A 0%
B 4%
B 7%
C 4%
C 7%
C 10%
UV TYPE & %

INTERNATIONAL SEARCH REPORT

Interi onal application No.
PCT/IL 96/00165

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08L 75/04, C08L 69/00
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0320946 A2 (THE DOW CHEMICAL COMPANY), 21 June 1989 (21.06.89), abstract, examples 1-4	1-2,5-8, 11-12
Y	--	3-4,9-10
Y	Dialog Information Services, File 351, Dialog accession no. 010437866, WPI accession no. 95-339183/44, Teijin Kasei Ltd: "Polycarbonate resin layered plate, useful for window material - comprises thermoplastic urethane resin layer formed on surface of polycarbonate resin sheet, by thermo-compression bonding or co-extrusion"; & JP,A,7205385, 950808, 9544 (Basic)	3-4,9-10
	--	

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 March 1997	29. 04. 97
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+ 31-70) 340-3016	Authorized officer JACK HEDLUND

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IL 96/00165

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9322383 A1 (THE DOW CHEMICAL COMPANY), 11 November 1993 (11.11.93), page 3, line 8 - line 31, abstract, exemple 1	1-2,5-8, 11-12
A	EP 0218252 A2 (MONTEDIPE S.P.A.), 15 April 1987 (15.04.87), column 6, line 1 - line 11	1-12
A	EP 0658581 A2 (WOLFF WALSRODE AG), 21 June 1995 (21.06.95), page 7, line 6 - line 12, claims 1,5	5-6,11-12
A	EP 0247480 A2 (BAYER AG), 2 December 1987 (02.12.87), abstract	6,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

04/03/97

International application No.
PCT/IL 96/00165

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0320946 A2	21/06/89	AT 124968 T	15/07/95
		AU 2641188 A	22/06/89
		CA 1334607 A	28/02/95
		DE 3854150 D,T	01/02/96
		ES 2074434 T	16/09/95
		JP 1259023 A	16/10/89
		US 4822827 A	18/04/89
WO 9322383 A1	11/11/93	CA 2133582 A	11/11/93
		EP 0638109 A	15/02/95
		JP 7506142 T	06/07/95
		US 5319039 A	07/06/94
EP 0218252 A2	15/04/87	AU 604653 B	03/01/91
		AU 6361786 A	16/04/87
		CA 1292349 A	26/11/91
		DE 3683117 A	06/02/92
		JP 62128728 A	11/06/87
		US 4868058 A	19/09/89
EP 0658581 A2	21/06/95	CA 2135958 A	20/05/95
		DE 4339475 A	24/05/95
EP 0247480 A2	02/12/87	CA 1312404 A	05/01/93
		DE 3617978 A	03/12/87
		DE 3786302 A	29/07/93
		ES 2055693 T	01/09/94
		JP 6027251 B	13/04/94
		JP 6263976 A	20/09/94
		JP 8030142 B	27/03/96
		JP 63010653 A	18/01/88
		US 5001177 A	19/03/91